Unusual π-π interactions directed by $[\{(C_6H_6)Ru\}_2W_8O_{30}(OH)_2]^{6-}$ hybrid anion

Anna A. Mukhacheva†, Vladislav Yu. Komarov†, Vasily V. Kokovkin†, Alexander Novikov‡, Pavel A. Abramov†,‖, Maxim N. Sokolov†*

Supporting information

Table of contents

Table S1. Experimental details

Experiments were carried out at 150 K with Mo *K*a radiation. H-atom parameters were constrained.

	(2)	(3)	(4)	(5)
Chemical formula	$C_{12}H_{12}Na_{3.80}O_{45}Ru_2W_8$	$C_{12}H_{12}Na_6O_{52}Ru_2W_8$	$C_{12}H_{54}Na_4O_{48.95}Ru_2W_8$	$C_{12}H_{12}Na_{4.20}O_{54.40}Ru_2W_8$
M_r	2636.52	2799.10	2746.65	2796.11
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$	Monoclinic, $I2/a$	Monoclinic, $C2/c$
a, b, c (Å)	10.3129 (4), 16.4452 (6), 14.8941 (5)	25.8211 (11), 16.9966 (7), 17.3342 (7)	20.5086 (8), 17.1615 (7), 17.3902 (8)	25.5718 (4), 17.0393 (3), 17.3183 (3)
β (°)	103.446 (2)	127.743 (1)	93.080 (4)	127.656 (1)
V (Å^3)	2456.77 (16)	6015.7 (4)	6111.8 (4)	5974.13 (19)
Z	2	4	4	4
μ (mm^{-1})	19.39	15.87	15.60	15.97
Crystal size (mm)	0.46 × 0.09 × 0.02	0.20 × 0.07 × 0.04	0.30 × 0.10 × 0.10	0.11 × 0.08 × 0.08
Diffractometer	Bruker D8 Venture	Bruker D8 Venture	New Xcalibur, AtlasS2	Bruker D8 Venture
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)	Multi-scan *SADABS* (Bruker-AXS, 2004)	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan *SADABS* (Bruker-AXS, 2004)
T_{min}, T_{max}	0.619, 0.746	0.615, 0.746	0.315, 1.000	0.537, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	83359, 8082, 5083	59528, 10009, 8603	15633, 7178, 5973	43675, 11281, 8655
R_{int}	0.201	0.044	0.034	0.062
θ values (°)	θ_{max} = 31.5, θ_{min} = 1.9	θ_{max} = 31.5, θ_{min} = 2.0	θ_{max} = 29.5, θ_{min} = 3.3	θ_{max} = 33.1, θ_{min} = 2.0
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.736	0.736	0.693	0.769
Range of h, k, l	$-15 \le h \le 15$, $-24 \le k \le 24$, $-21 \le l \le 21$	$-37 \le h \le 37$, $-24 \le k \le 24$, $-25 \le l \le 25$	$-28 \le h \le 27$, $-23 \le k \le 22$, $-23 \le l \le 13$	$-39 \le h \le 38$, $-26 \le k \le 26$, $-25 \le l \le 26$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.129, 0.94	0.032, 0.081, 1.03	0.037, 0.097, 1.06	0.040, 0.089, 1.07
No. of reflections, parameters, restraints	8082, 330, 0	10009, 363, 0	7178, 354, 0	11281, 366, 36

Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 125.0742P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 99.4997P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.38, -2.98	2.94, -1.97	1.91, -2.54	4.38, -2.78

	(6)
Chemical formula	$C_{12}H_{12}Na_{0.50}O_{38.70}Ru_2W_8$
M_r	2459.85
Crystal system, space group	Monoclinic, *C*2/*c*
a, *b*, *c* (Å)	24.1881 (7), 18.2571 (6), 16.5476 (6)
b (°)	125.354 (1)
V (Å^3)	5959.9 (3)
Z	4
μ (mm^{-1})	15.94
Crystal size (mm)	0.11 × 0.08 × 0.08
Diffractometer	Bruker D8 Venture
Absorption correction	Multi-scan *SADABS* (Bruker-AXS, 2004)
T_{min}, T_{max}	0.495, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29760, 6095, 4039
R_{int}	0.088
θ values (°)	θ_{max} = 26.4, θ_{min} = 2.1
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.625
Range of *h*, *k*, *l*	$-30 \le h \le 30$, $-22 \le k \le 21$, $-20 \le l \le 20$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.053, 0.152, 1.05
No. of reflections, parameters, restraints	6095, 289, 36
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.02, -1.35

Computer programs: *APEX2* (Bruker-AXS, 2004), *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), *SAINT* (Bruker-AXS, 2004), *SHELXS2014* (Sheldrick, 2014), *SHELXL2014* (Sheldrick, 2014), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014).

Table S2. Selected geometric parameters (Å)

2			
O1—Ru1	2.096 (8)	O6—W3	2.127 (8)
O2—Ru1	2.088 (8)	O7—W2	1.885 (8)
O15—Ru1	2.101 (8)	O7—W3	1.954 (7)
O1—W1	2.020 (8)	O8—W2	1.762 (8)
O1—W4	2.124 (8)	O9—W2	1.734 (8)
O2—W1	2.016 (8)	O10—W3	1.726 (9)
O2—W2	2.133 (9)	O11—W3	1.753 (9)
O3—W1	1.728 (8)	O12—W3	1.933 (7)
O4—W1	1.855 (8)	O12—W4^{i}	1.868 (7)
O4—W3^{i}	2.166 (8)	O13—W4	1.744 (8)
O5—W1	2.275 (7)	O14—W4	1.744 (9)
O5—W2	2.235 (7)	O15—W2	2.031 (8)
O5—W4	2.243 (7)	O15—W4	2.050 (8)
O6—W1	1.841 (8)		
3			
O1—Ru1	2.084 (4)	O6—W2	1.955 (4)
O2—Ru1	2.076 (4)	O6—W3	1.857 (4)
O13—Ru1	2.112 (4)	O7—W3	1.741 (4)
O1—W1	2.008 (4)	O8—W3	1.755 (5)
O1—W4	2.146 (4)	O9—W2	1.759 (4)
O2—W1	2.016 (4)	O10—W2	1.751 (5)
O2—W3	2.126 (4)	O11—W2^{ii}	1.917 (4)
O3—W1	1.829 (4)	O11—W4	1.890 (4)
O3—W2^{ii}	2.133 (4)	O12—W4	1.751 (4)
O4—W1	1.842 (4)	O13—W3	2.040 (4)
O4—W2	2.155 (4)	O13—W4	2.031 (4)
O5—W1	2.304 (4)	O14—W4	1.746 (5)
O5—W3	2.220 (4)	O21—W1	1.737 (4)
O5—W4	2.224 (4)		
4			
O2—Ru1	2.110 (6)	O7—W2	1.724 (6)
O3—Ru1	2.079 (6)	O8—W4	1.738 (6)
O6—Ru1	2.069 (6)	O9—W4	1.756 (7)
O1—W2	2.311 (6)	O10—W1	1.956 (6)
O1—W3	2.220 (6)	O10—W4	1.857 (6)
O1—W4	2.224 (6)	O11—W1	2.154 (6)
O2—W3	2.047 (6)	O11—W2	1.838 (6)

O2—W4	2.039 (6)	O12—W1	1.756 (7)
O3—W2	2.027 (6)	O13—W1	1.926 (6)
O3—W3	2.143 (6)	O13—W3^{i}	1.882 (6)
O4—W3	1.743 (6)	O14—W1	1.730 (7)
O5—W3	1.738 (6)	O15—W1	2.117 (6)
O6—W2	2.017 (6)	O15—W2^{i}	1.839 (6)
O6—W4	2.124 (6)		
5			
Ru1—O4	2.115 (4)	O7—W2	1.735 (4)
Ru1—O5	2.094 (4)	O8—W2	1.832 (4)
Ru1—O6	2.078 (4)	O8—W3^{iii}	2.163 (4)
O1—W1	1.734 (5)	O9—W2	1.821 (4)
O2—W1	1.731 (5)	O9—W3	2.140 (4)
O3—W1	2.227 (4)	O10—W3	1.749 (5)
O3—W2	2.305 (4)	O11—W1	1.891 (4)
O3—W4	2.227 (4)	O11—W3	1.915 (4)
O4—W1	2.036 (4)	O12—W3	1.760 (5)
O4—W4	2.036 (4)	O13—W3^{iii}	1.953 (4)
O5—W1	2.158 (5)	O13—W4	1.863 (4)
O5—W2	2.016 (4)	O14—W4	1.743 (5)
O6—W2	2.007 (4)	O15—W4	1.742 (5)
O6—W4	2.131 (4)		
6			
O1—Ru1	2.091 (10)	O8—W2	1.877 (12)
O2—Ru1	2.088 (10)	O8—W3	1.927 (12)
O13—Ru1	2.112 (11)	O9—W3	1.738 (13)
O1—W1	2.079 (10)	O10—W3	1.745 (12)
O1—W4	2.193 (11)	O11—W3^{ii}	1.907 (11)
O2—W1	1.982 (11)	O11—W4	1.890 (11)
O2—W2	2.162 (10)	O12—W4	1.731 (12)
O3—W1	1.724 (10)	O13—W2	2.061 (11)
O4—W1	1.826 (10)	O13—W4	2.023 (11)
O4—W3^{ii}	2.170 (10)	O14—W4^{ii}	1.766 (11)
O5—W1	1.827 (10)	O15—W1	2.301 (10)
O5—W3	2.147 (10)	O15—W2	2.239 (10)
O6—W2	1.765 (11)	O15—W4	2.215 (11)
O7—W2	1.751 (14)		

Symmetry code(s): (i) -*x*+1, -*y*+1, -*z*+1; (ii) -*x*+3/2, -*y*+1/2, -*z*+1; (iii) -*x*+1/2, -*y*+3/2, -*z*+1.

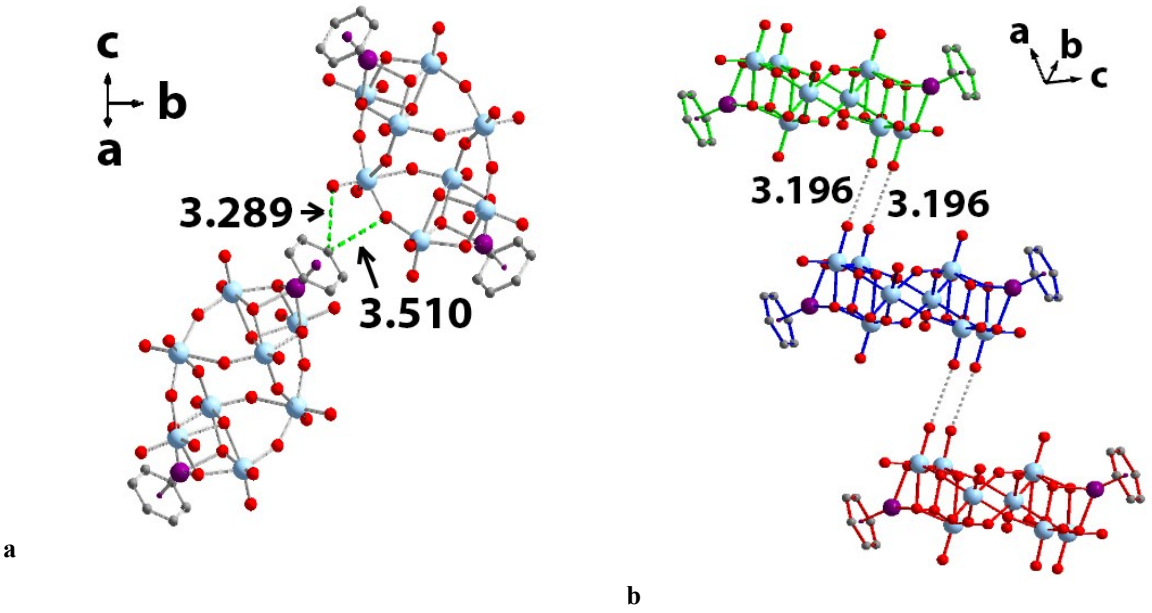


Figure S1. Location of polyanions (a) in the plane of the layer and (b) in adjacent layers in structures of type A. The gray dotted line marks the shortest distances O… O. Green dotted line - contacts edge C_6H_6…O, red - plane C_6H_6…O.

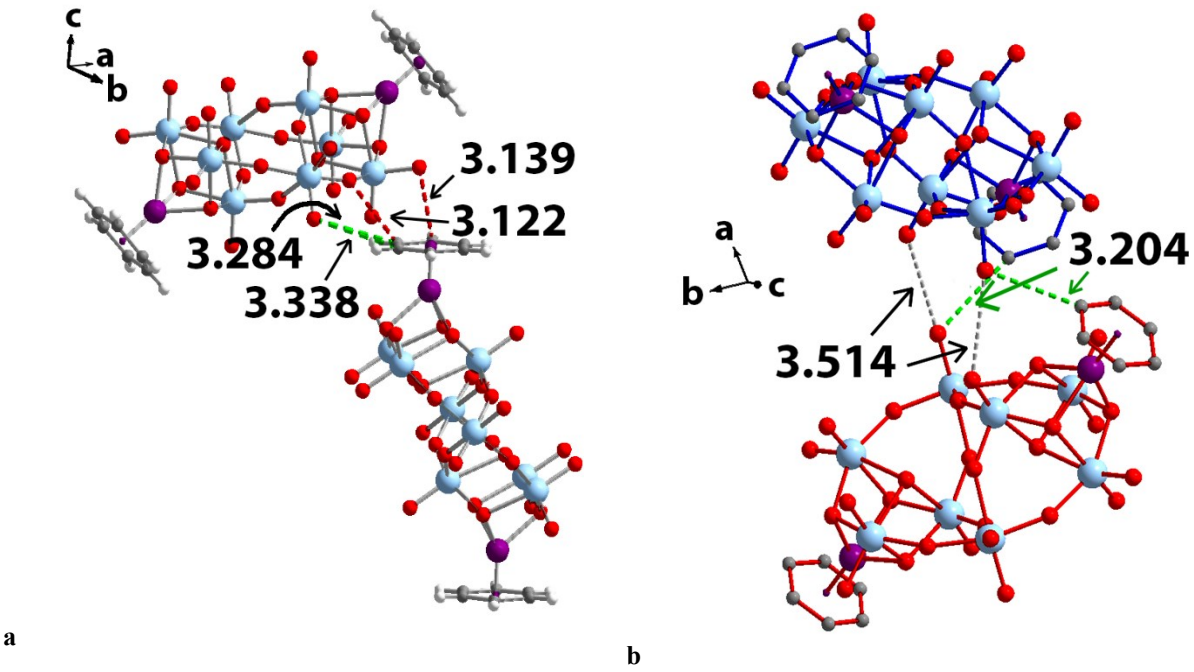
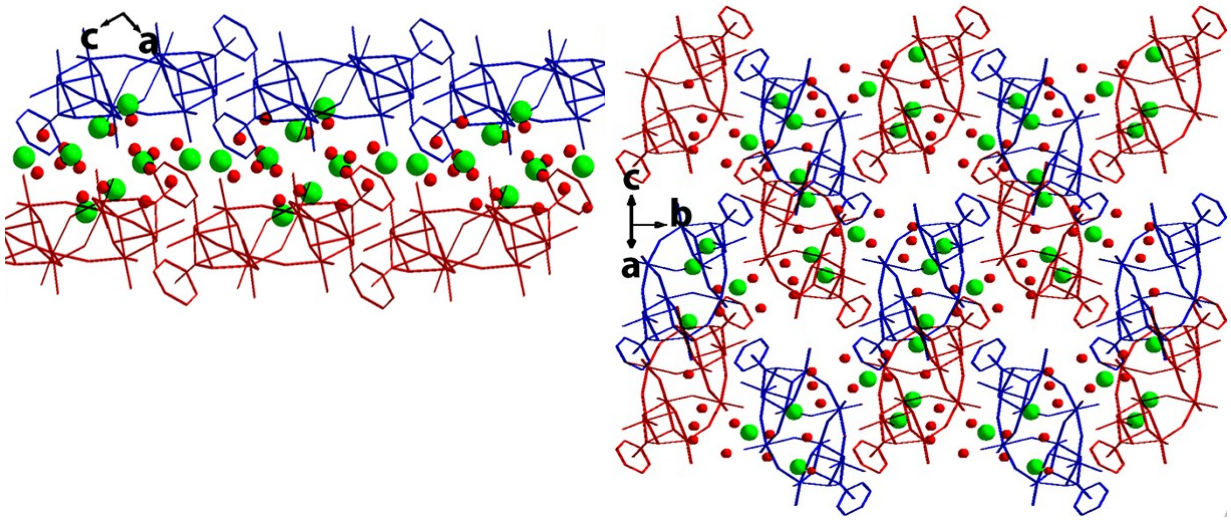


Figure S2. Location of polyanions (a) in the plane of the layer and (b) the nearest in adjacent layers in structures of type B. Gray dotted line marks the shortest distances O… O. Green dotted line - contacts edge C_6H_6…O, red - plane C_6H_6…O.

1



2

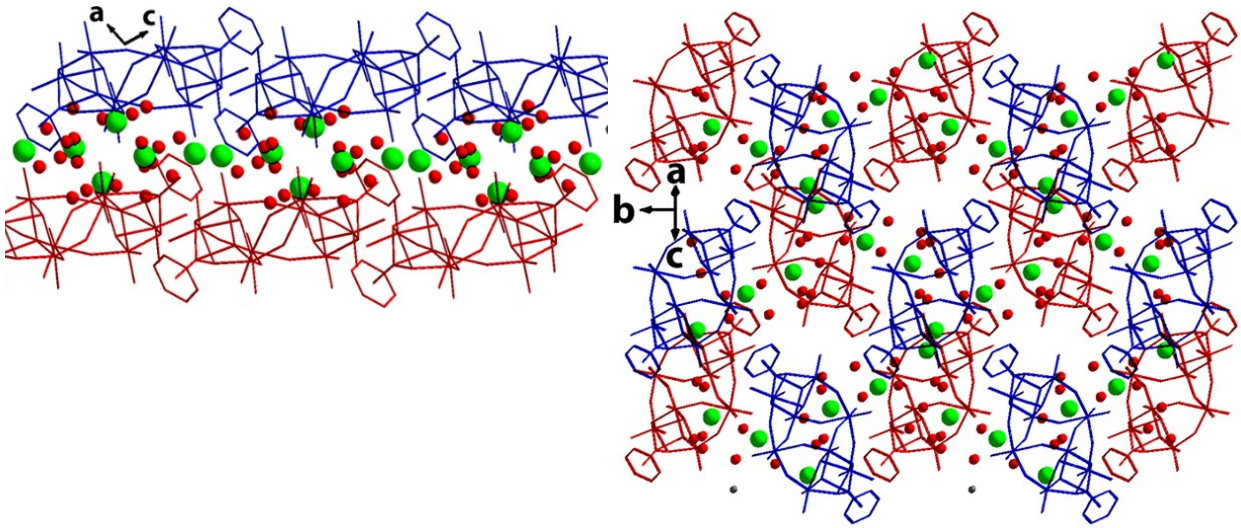


Figure S3. Relative location of anionic and water-cationic layers in structures of type A.

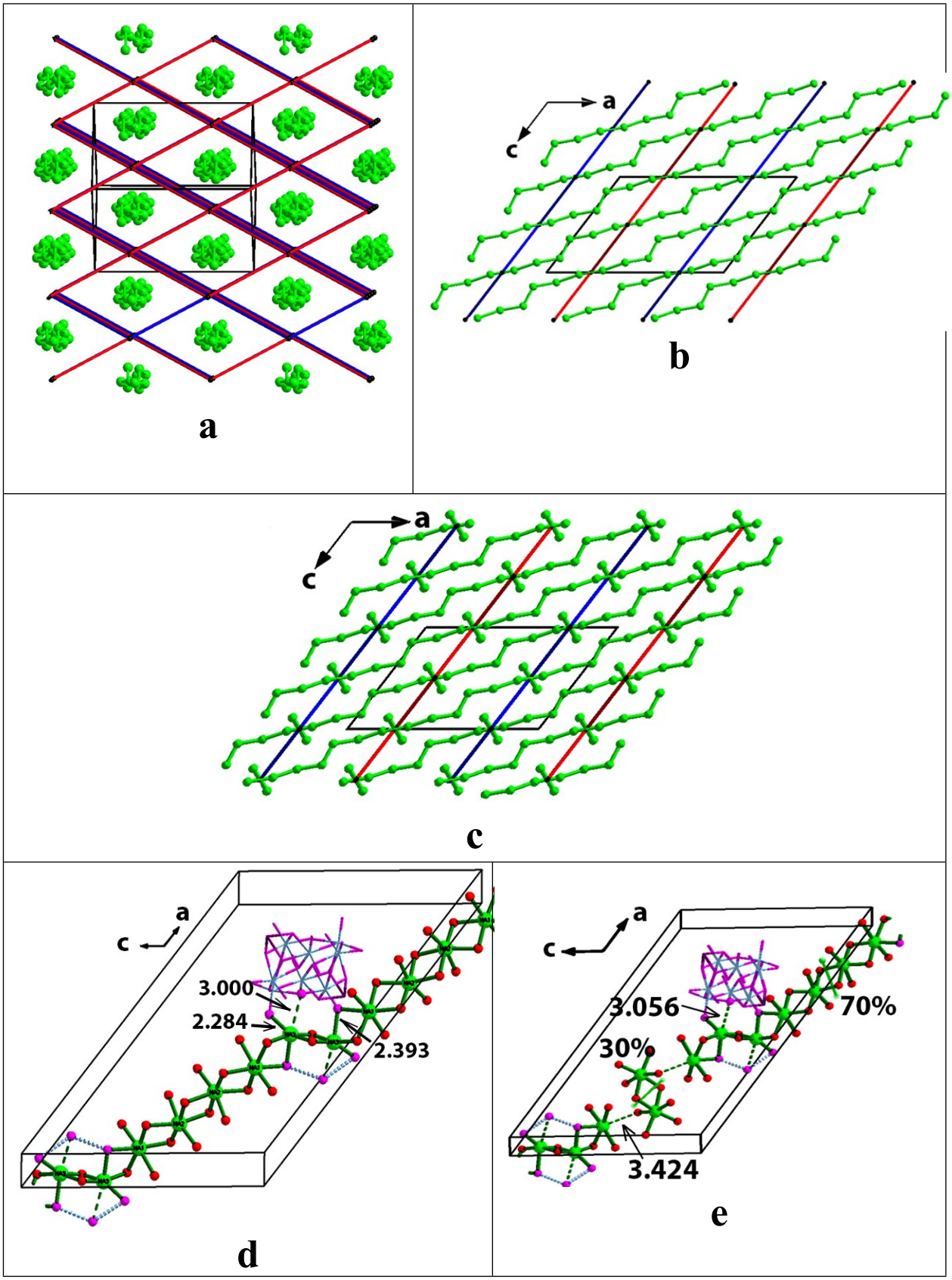


Figure S4. Arrangement of Na^+ coordination chains relative to polyanionic layers in structures **5** and **3**. (a) general view along the direction of the chains, (b, c) - view perpendicular to the direction of layers and chains for **5** and **3**, respectively, (d, e) - coordination structure of single cationic chains for **5** and **3**, respectively. Green balls show Na atoms, red - coordinated water molecules, pink - oxygen atoms of polyanions. The belonging of oxygen atoms to one polyanion is shown by blue dashed lines.

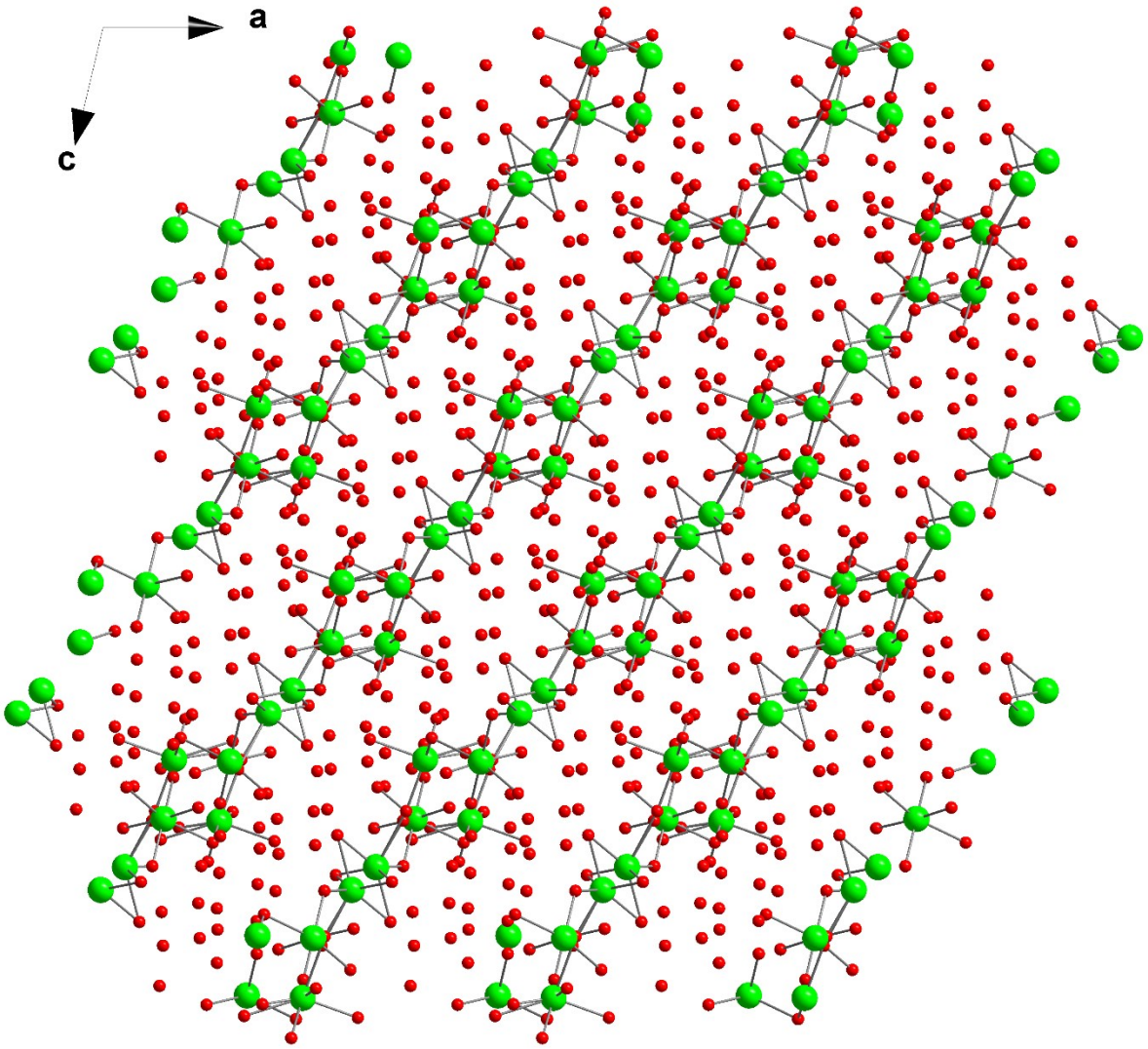


Fig. S1. Layers of hydrated Na+ cations in the crystal structure of 2.

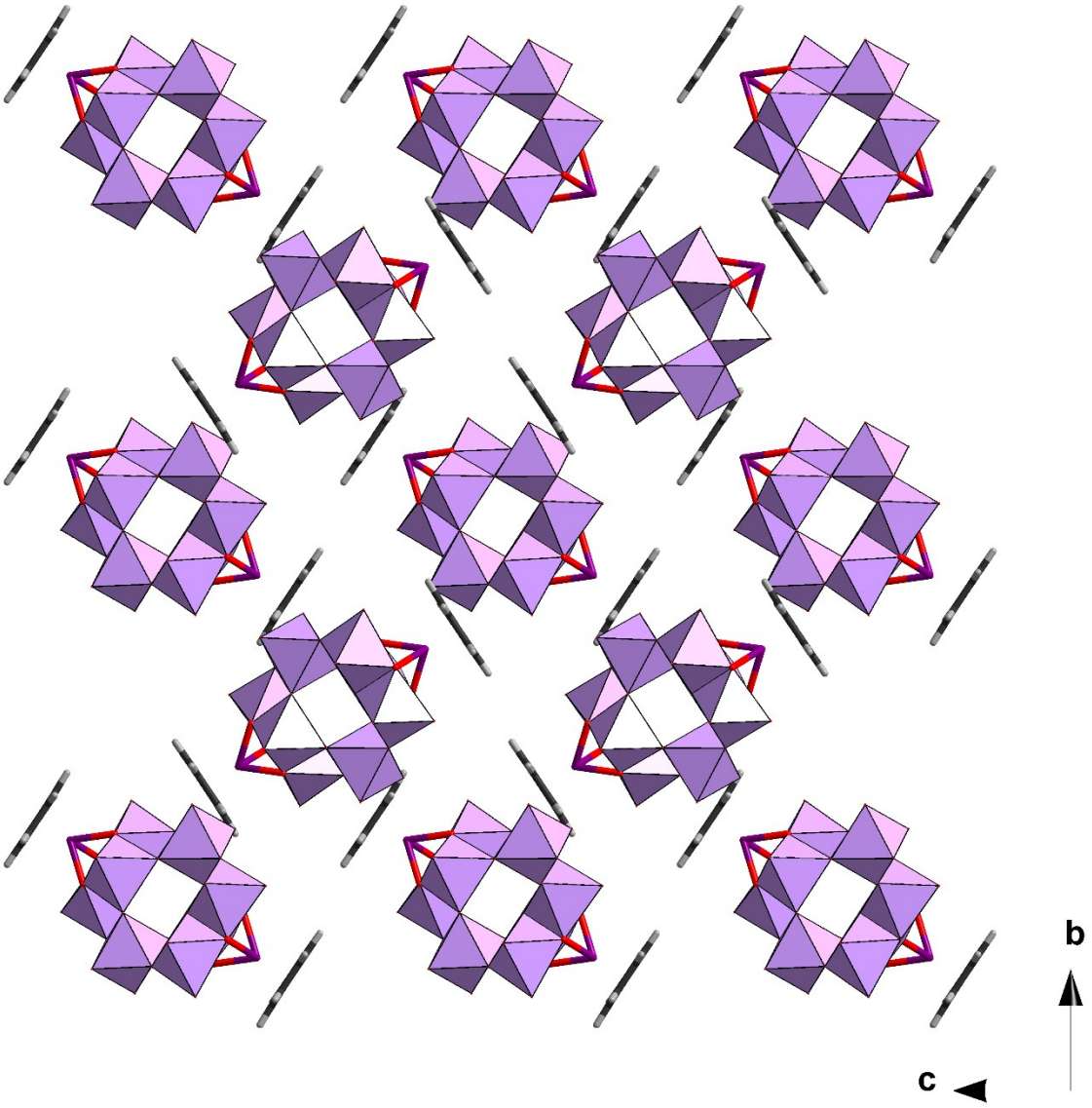


Fig. S2. Pseudo layered packing of POM hybrid anions in the crystal structure of 2.

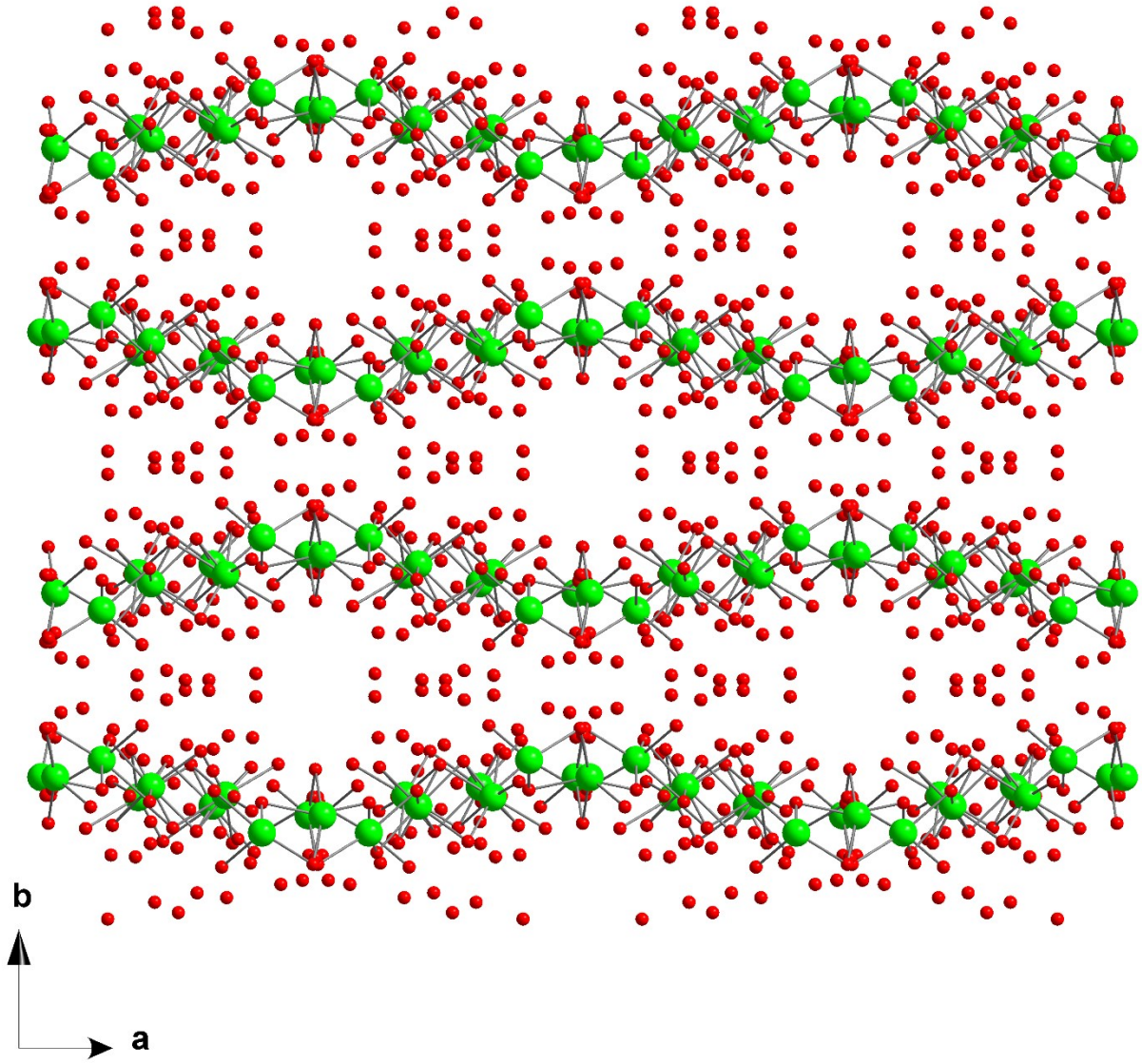


Fig. S3. Crimped pseudo layers of hydrated sodium cations in the crystal structure of **3**.

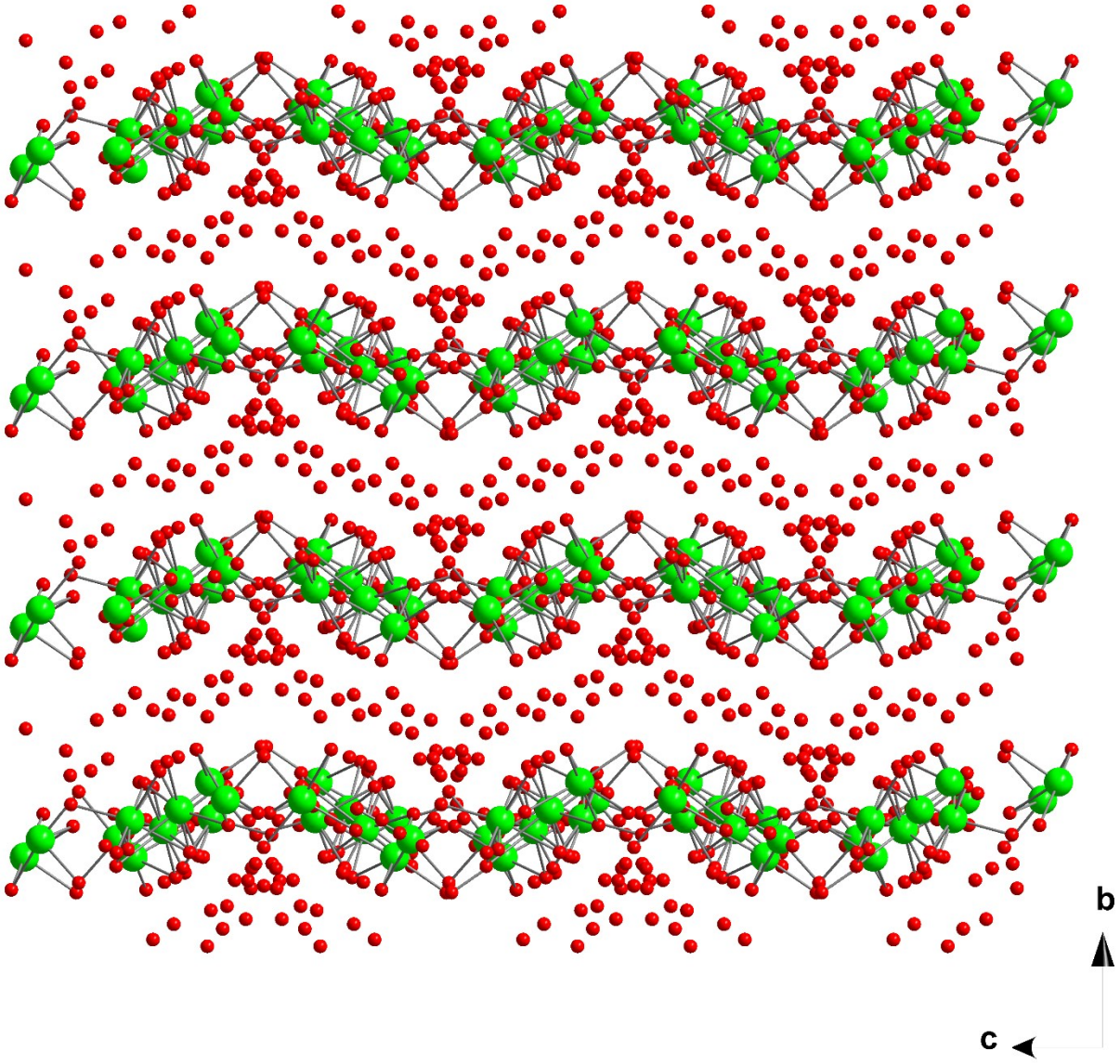


Fig. S4. Crimped pseudo layers of hydrated sodium cations in the crystal structure of 3.

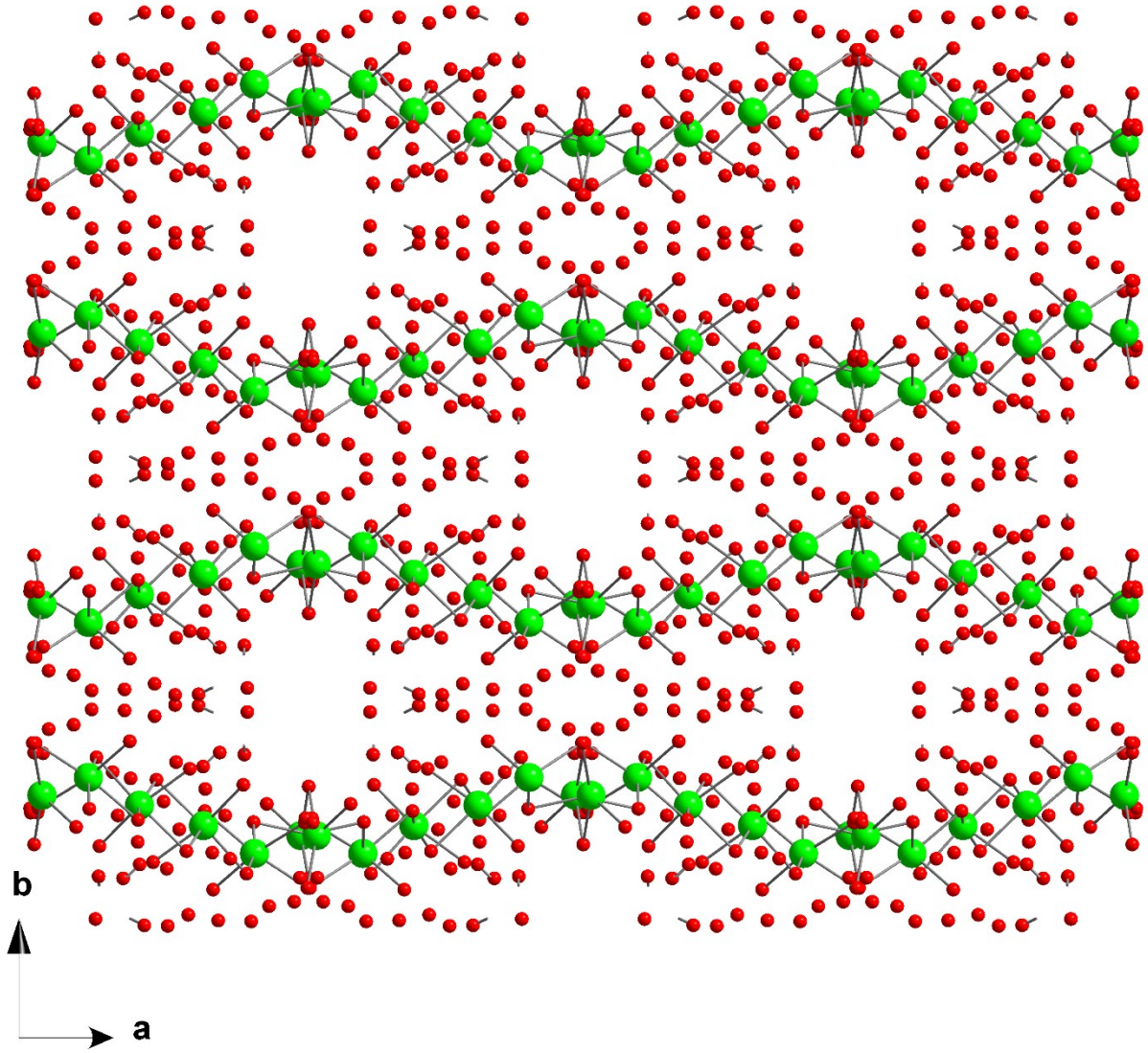


Fig. S5. Crimped pseudo layers of hydrated sodium cations in the crystal structure of 5.

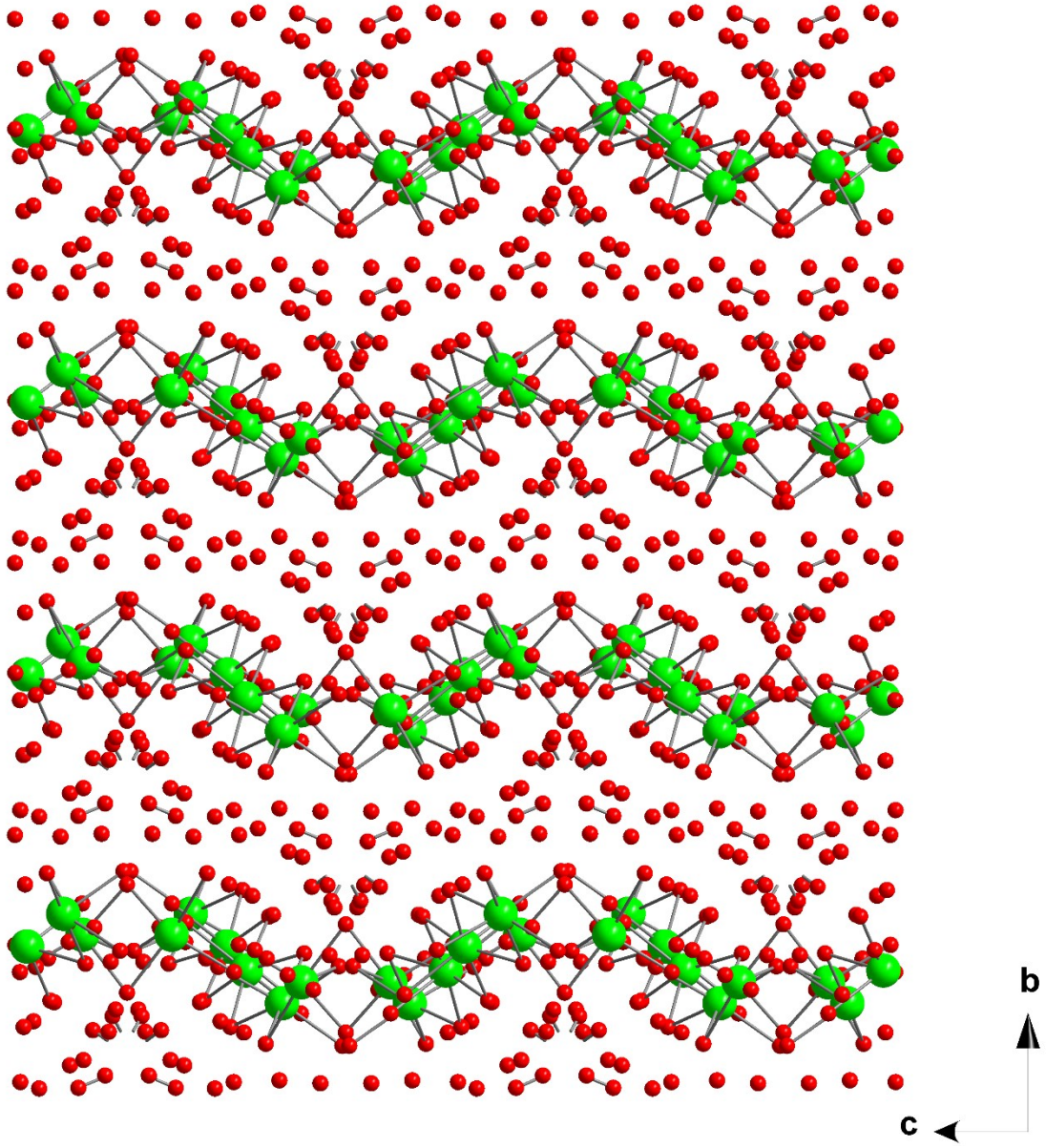


Fig. S6. Crimped pseudo layers of hydrated sodium cations in the crystal structure of 5.

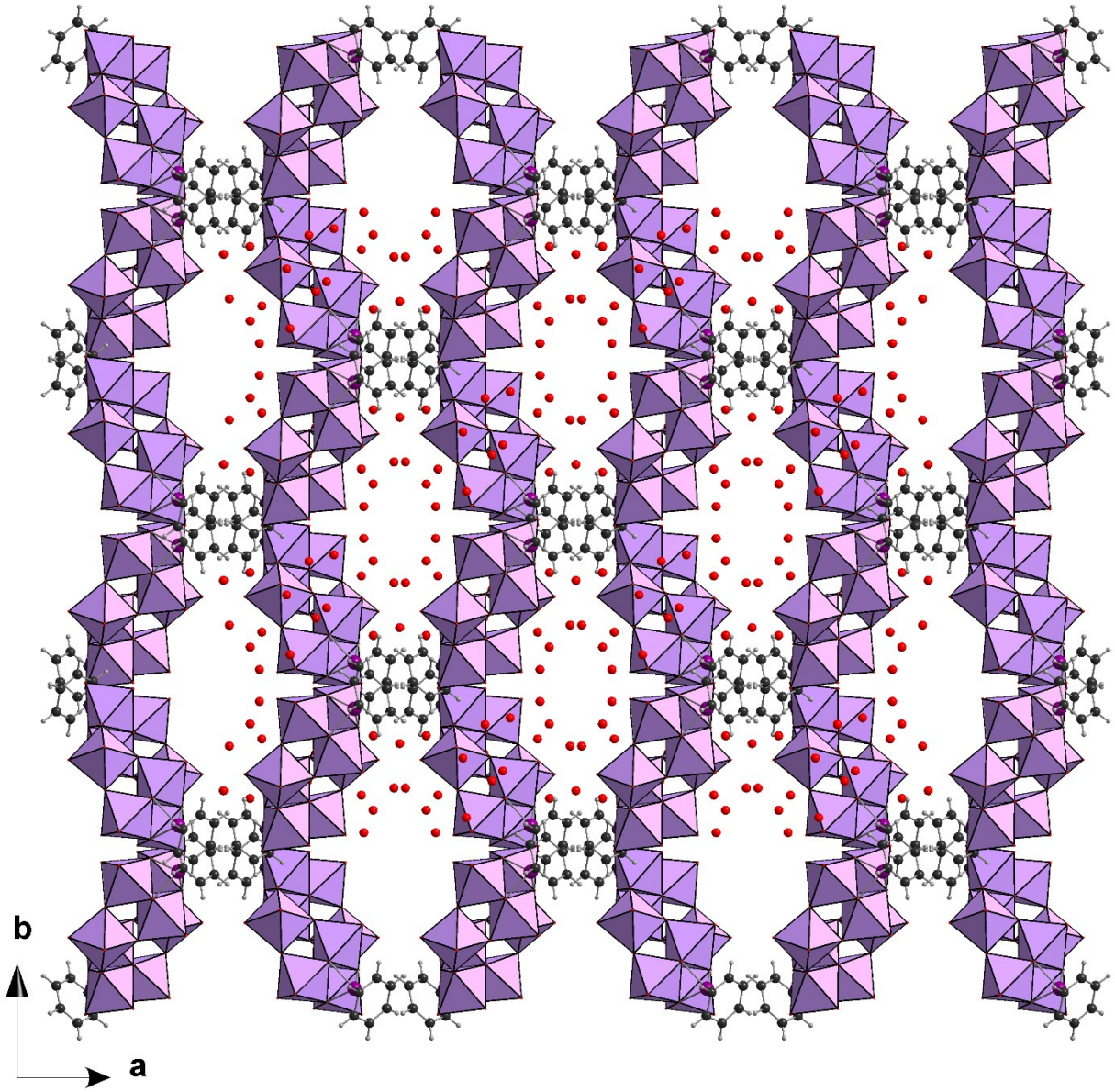


Fig. S7. Crystal packing of 6.

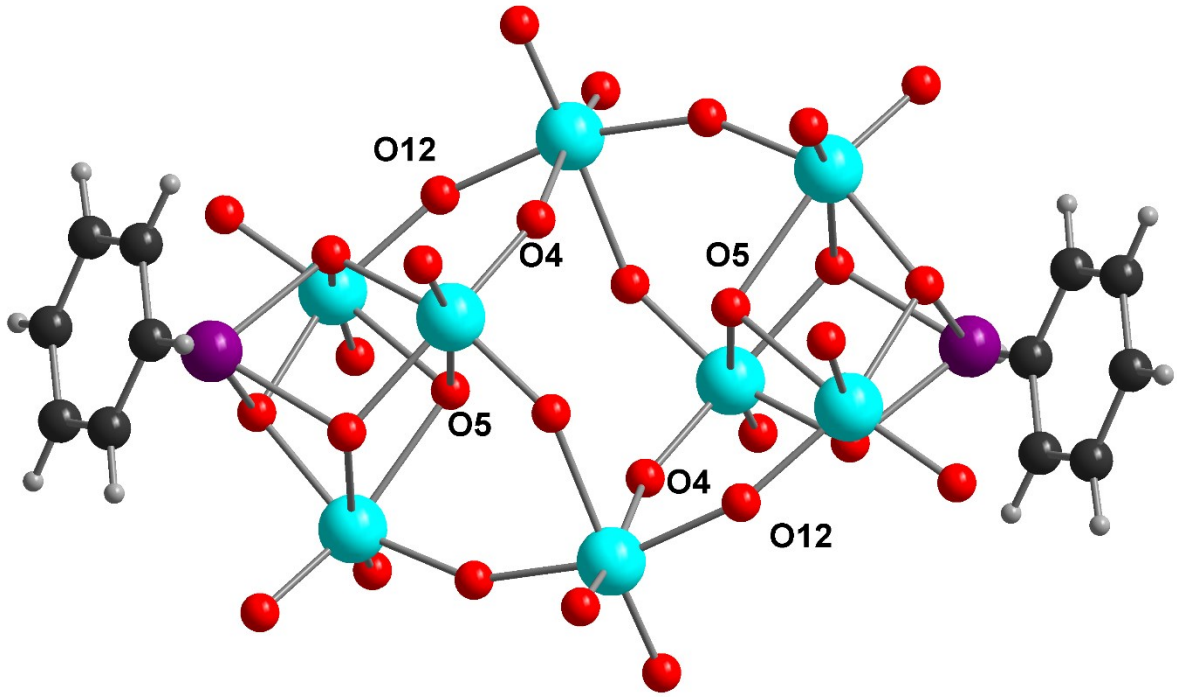
BVS part

Complex 2

O4 -1,20 partially protonated

O5 -1,20 partially protonated

O12 -0,89 - protonated

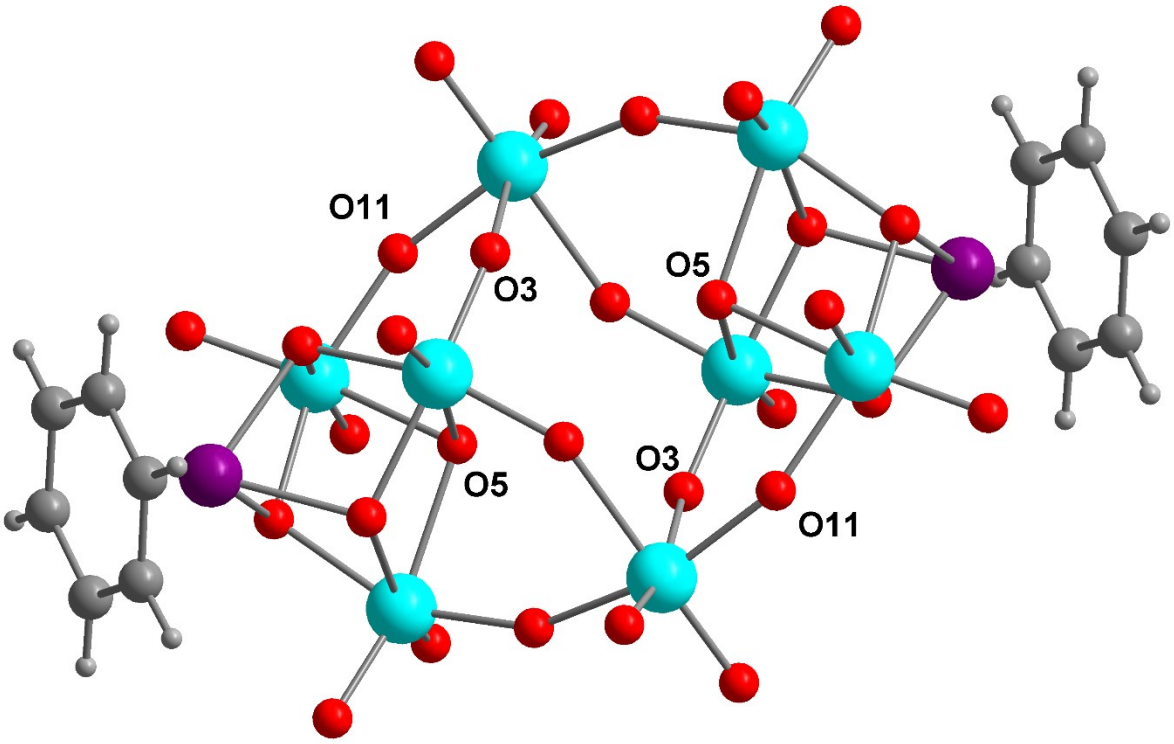


Complex 3

O3 -1,28 partially protonated

O5 -1,24 partially protonated

O11 -1,08 protonated

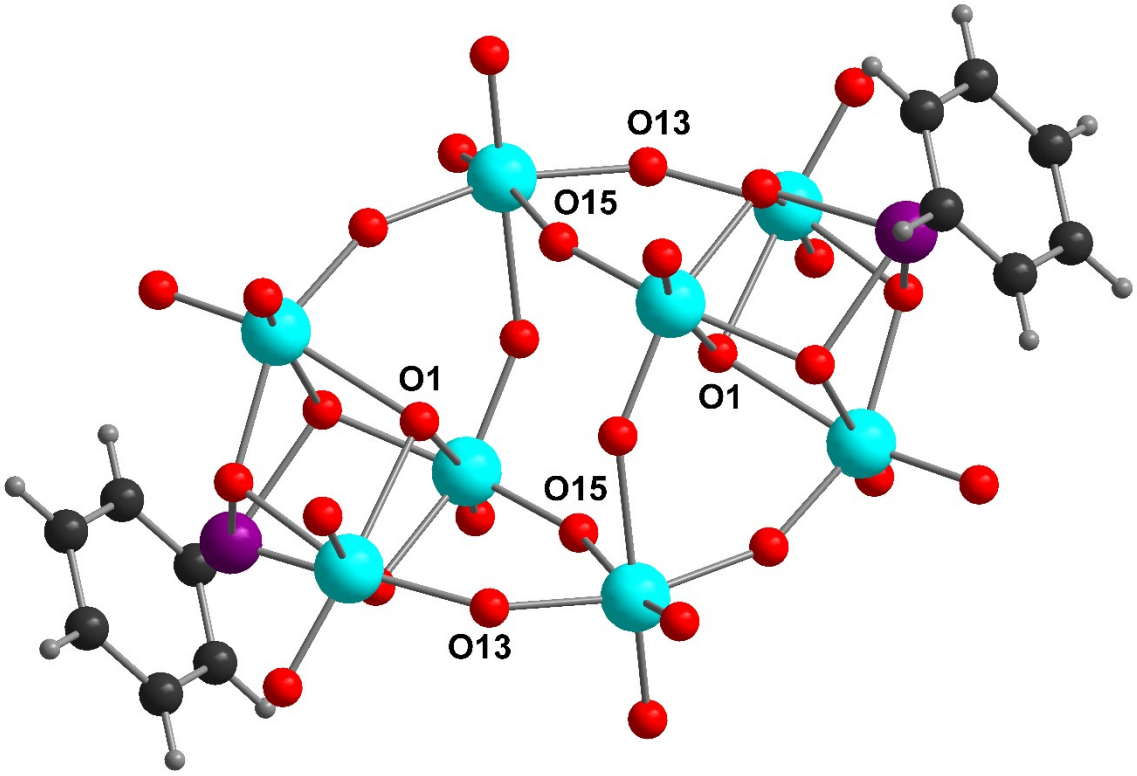


Complex 4

O13 -0,99 protonated

O15 -0,60 protonated

O1 -1,17 partially protonated

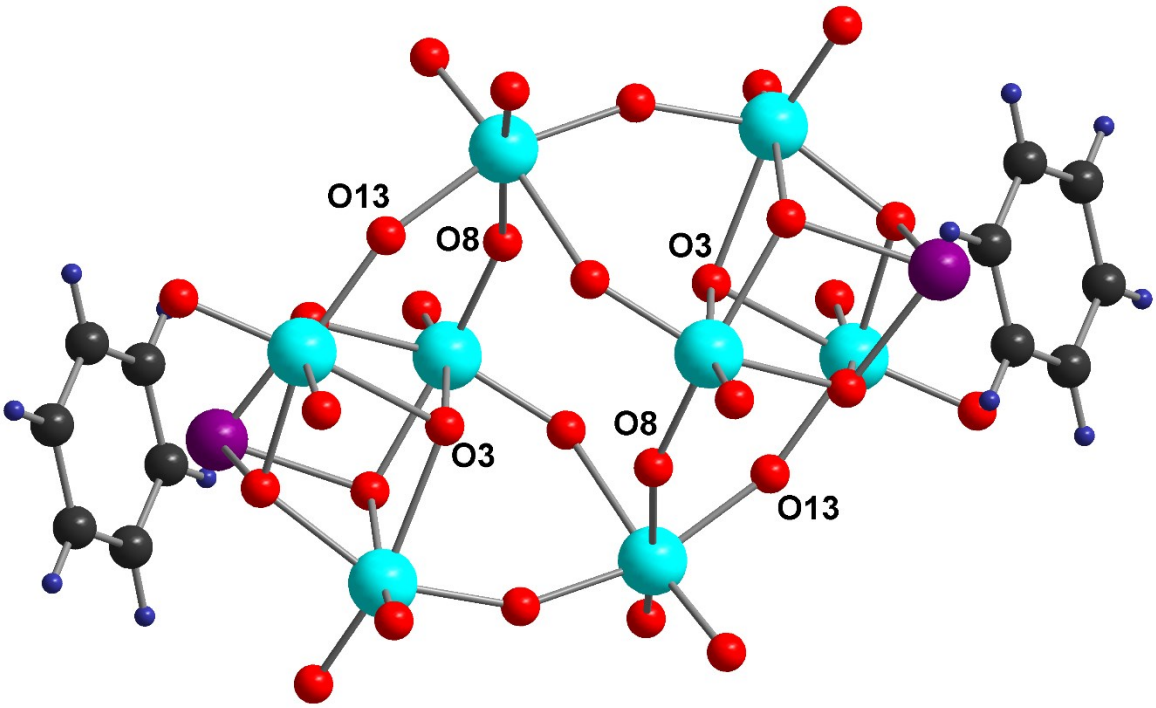


Complex 5

O3 -1,23 partially protonated

O8 -1,27 partially protonated

O13 -1,17 partially protonated



Complex 6

O4 -1,28 partially protonated

O11 -1,00 protonated

O14 0,00 – H_2O! wrong value d(W4-O14) = 1.76!

O15 -1,19 partially protonated

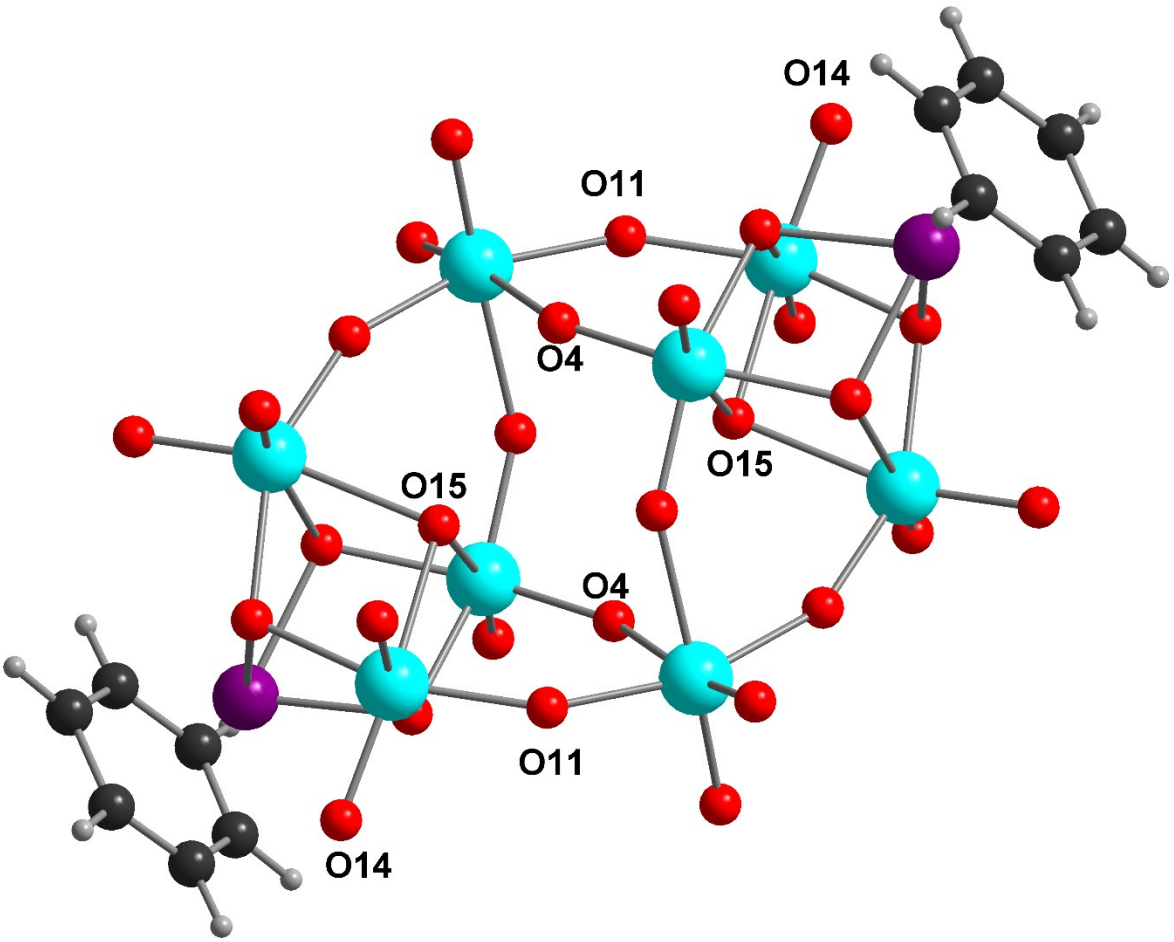


Table S3. Cartesian atomic coordinates for model structures

Atom	X	Y	Z
pH5			
C	13.067997	7.249894	0.863750
H	13.177963	6.387849	0.480799
C	11.862562	7.677111	1.202503
H	11.105318	7.132757	1.025947
C	11.690152	8.940502	1.827372
H	10.816035	9.209009	2.082678
C	12.699595	9.756594	2.064903
H	12.544616	10.607539	2.456479
C	13.998002	9.356764	1.738298
H	14.753656	9.899328	1.936461
C	14.136198	8.045904	1.066192
H	14.993792	7.759213	0.772193
O	11.894766	6.802595	4.297158
O	14.291068	6.311479	3.742469
O	12.452390	4.259381	3.105453
O	11.697587	4.553321	5.754737
O	14.345448	3.981874	5.135266
O	16.416287	8.186484	4.009691
O	15.716310	8.367229	6.680570
O	16.200255	5.853226	5.664313
O	17.017141	3.452418	4.598121
O	17.655678	4.153490	7.131339
O	10.952409	6.899358	6.835775
O	12.703255	8.951456	7.436351
O	13.691018	8.610048	4.823506
O	13.592055	6.503179	6.217653
Ru	13.107267	7.834852	2.944039
W	12.979620	5.044437	4.546701

W	15.352300	7.468797	5.226095
W	16.271340	3.972928	6.083367
W	12.115948	8.145223	6.015347
O	10.968028	9.278258	5.293171
C	13.639272	1.878656	12.632350
H	13.529307	2.740701	13.015302
C	14.844707	1.451439	12.293598
H	15.601951	1.995793	12.470154
C	15.017117	0.188048	11.668728
H	15.891234	-0.080459	11.413423
C	14.007675	-0.628044	11.431197
H	14.162653	-1.478989	11.039621
C	12.709267	-0.228214	11.757803
H	11.953614	-0.770778	11.559639
C	12.571072	1.082646	12.429908
H	11.713477	1.369337	12.723907
O	14.812503	2.325955	9.198942
O	12.416201	2.817071	9.753632
O	14.254879	4.869169	10.390648
O	15.009682	4.575229	7.741363
O	12.361821	5.146676	8.360834
O	10.290982	0.942066	9.486409
O	10.990959	0.761321	6.815531
O	10.507014	3.275324	7.831787
O	9.690128	5.676132	8.897979
O	9.051591	4.975060	6.364761
O	15.754861	2.229192	6.660325
O	14.004014	0.177094	6.059749
O	13.016251	0.518502	8.672594
O	13.115214	2.625371	7.278447

Ru	13.600002	1.293698	10.552061
W	13.727649	4.084113	8.949399
W	11.354969	1.659753	8.270005
W	10.435929	5.155622	7.412733
W	14.591322	0.983327	7.480753
O	15.739241	-0.149708	8.202930
C	10.548828	16.378444	-12.632350
H	10.658793	15.516399	-13.015302
C	9.343393	16.805661	-12.293598
H	8.586149	16.261307	-12.470154
C	9.170983	18.069052	-11.668728
H	8.296866	18.337559	-11.413423
C	10.180425	18.885144	-11.431197
H	10.025447	19.736089	-11.039621
C	11.478833	18.485314	-11.757803
H	12.234486	19.027878	-11.559639
C	11.617028	17.174454	-12.429908
H	12.474623	16.887763	-12.723907
O	9.375597	15.931145	-9.198942
O	11.771899	15.440029	-9.753632
O	9.933221	13.387931	-10.390648
O	9.178418	13.681871	-7.741363
O	11.826279	13.110424	-8.360834
O	13.897118	17.315034	-9.486409
O	13.197141	17.495779	-6.815531
O	13.681086	14.981776	-7.831787
O	14.497972	12.580968	-8.897979
O	15.136509	13.282040	-6.364761
O	8.433239	16.027908	-6.660325
O	10.184086	18.080006	-6.059749

O	11.171849	17.738598	-8.672594
O	11.072886	15.631729	-7.278447
Ru	10.588098	16.963402	-10.552061
W	10.460451	14.172987	-8.949399
W	12.833131	16.597347	-8.270005
W	13.752171	13.101478	-7.412733
W	9.596778	17.273773	-7.480753
O	8.448859	18.406808	-8.202930
C	11.120103	11.007206	-0.863750
H	11.010137	11.869251	-0.480799
C	12.325538	10.579989	-1.202503
H	13.082782	11.124343	-1.025947
C	12.497948	9.316598	-1.827372
H	13.372065	9.048091	-2.082678
C	11.488505	8.500506	-2.064903
H	11.643484	7.649561	-2.456479
C	10.190098	8.900336	-1.738298
H	9.434444	8.357772	-1.936461
C	10.051902	10.211196	-1.066192
H	9.194308	10.497887	-0.772193
O	12.293334	11.454505	-4.297158
O	9.897032	11.945621	-3.742469
O	11.735710	13.997719	-3.105453
O	12.490513	13.703779	-5.754737
O	9.842652	14.275226	-5.135266
O	7.771813	10.070616	-4.009691
O	8.471790	9.889871	-6.680570
O	7.987845	12.403874	-5.664313
O	7.170959	14.804682	-4.598121
O	6.532422	14.103610	-7.131339

O	13.235691	11.357742	-6.835775
O	11.484845	9.305644	-7.436351
O	10.497082	9.647052	-4.823506
O	10.596045	11.753921	-6.217653
Ru	11.080833	10.422248	-2.944039
W	11.208480	13.212663	-4.546701
W	8.835800	10.788303	-5.226095
W	7.916760	14.284172	-6.083367
W	12.072152	10.111877	-6.015347
O	13.220072	8.978842	-5.293171
pH6			
Ru	8.18710400	9.50792900	9.93921500
O	6.10115100	8.07833200	12.36437700
O	7.90901200	8.33051400	14.38260300
O	8.76396500	10.81314000	13.21170300
O	8.80253700	8.72923300	11.80634900
O	7.02472200	10.53369500	11.34978000
O	9.41403800	10.97501300	10.73553700
O	7.58752800	13.02484100	10.06370900
O	9.47140100	13.29747000	12.10935700
O	6.83615900	12.77947500	12.76061900
O	4.21196200	12.35349300	13.63947900
O	6.16708800	10.46042600	13.94248800
O	5.16823900	11.80482700	16.11838800
O	11.38368800	11.40951500	12.56729700
O	11.49939700	9.11432200	10.96587800
O	10.84413900	8.90814600	13.62439800
C	9.10829200	8.05447700	8.63641700
H	9.87976300	7.51739800	8.76990600
C	7.83943900	7.58419200	9.01483500

H	7.74445800	6.72544600	9.40747000
C	6.71099600	8.40378300	8.80368900
H	5.84551400	8.08560800	9.03556600
C	6.86102300	9.67321100	8.25800000
H	6.10062900	10.23283200	8.14766900
C	8.10642000	10.12645600	7.87684100
H	8.19365700	10.98947900	7.48820900
C	9.22295500	9.34264800	8.05371000
H	10.07407500	9.66475900	7.78454000
W	7.24606600	9.20002900	13.02839000
W	8.07759400	12.24444100	11.53624600
W	5.72759900	12.23404700	14.50175000
W	10.47731500	9.82383800	12.18435500
O	7.72613300	12.26148000	15.31219400
O	5.81384600	14.14943500	14.85425400
W	11.46993500	13.32490300	12.91980100
Ru	9.01043100	16.05102100	17.48233600
O	11.09638300	17.48061800	15.05717400
O	9.28852200	17.22843600	13.03894700
O	8.43357000	14.74581000	14.20984800
O	8.39499800	16.82971700	15.61520200
O	10.17281200	15.02525500	16.07177100
O	7.78349700	14.58393700	16.68601400
O	9.61000700	12.53410900	17.35784200
O	10.36137500	12.77947500	14.66093200
O	12.98557200	13.20545800	13.78207200
O	11.03044600	15.09852400	13.47906300
O	12.02929500	13.75412300	11.30316300
O	5.69813800	16.44462800	16.45567300
O	6.35339500	16.65080400	13.79715300

C	8.08924200	17.50447300	18.78513300
H	7.31777100	18.04155200	18.65164500
C	9.35809500	17.97475800	18.40671600
H	9.45307600	18.83350400	18.01408100
C	10.48653800	17.15516700	18.61786200
H	11.35202000	17.47334200	18.38598500
C	10.33651200	15.88573900	19.16355100
H	11.09690500	15.32611800	19.27388100
C	9.09111500	15.43249400	19.54471000
H	9.00387700	14.56947100	19.93334200
C	7.97457900	16.21630200	19.36784100
H	7.12345900	15.89419100	19.63701100
W	9.95146800	16.35892100	14.39316100
W	9.11994100	13.31450900	15.88530400
W	6.72021900	15.73511200	15.23719600
Ru	6.80461300	7.53137100	3.77156000
O	8.89056600	8.96096800	1.34639800
O	7.08270500	8.70878600	-0.67182800
O	6.22775200	6.22616000	0.49907200
O	6.18918100	8.31006700	1.90442700
O	7.96699500	6.50560500	2.36099600
O	5.57767900	6.06428700	2.97523800
O	7.40418900	4.01445900	3.64706600
O	5.52031600	3.74183000	1.60141900
O	8.15555800	4.25982500	0.95015700
O	10.77975500	4.68580800	0.07129600
O	8.82462900	6.57887400	-0.23171200
O	9.82347800	5.23447300	-2.40761200
O	3.60802900	5.62978500	1.14347900
O	3.49232000	7.92497800	2.74489700

O	4.14757800	8.13115400	0.08637800
C	5.88342500	8.98482300	5.07435800
H	5.11195400	9.52190200	4.94087000
C	7.15227800	9.45510800	4.69594100
H	7.24725900	10.31385400	4.30330500
C	8.28072100	8.63551700	4.90708700
H	9.14620300	8.95369200	4.67521000
C	8.13069500	7.36608900	5.45277500
H	8.89108800	6.80646800	5.56310600
C	6.88529700	6.91284400	5.83393500
H	6.79806000	6.04982100	6.22256700
C	5.76876200	7.69665200	5.65706600
H	4.91764200	7.37454100	5.92623600
W	7.74565100	7.83927100	0.68238500
W	6.91412400	4.79485900	2.17452900
W	9.26411800	4.80525300	-0.79097500
W	4.51440200	7.21546200	1.52642100
O	7.26558400	4.77782000	-1.60141900
O	9.17787100	2.88986500	-1.14347900
W	3.52178200	3.71439700	0.79097500
Ru	5.98128700	0.98827900	-3.77156000
O	3.89533400	-0.44131800	-1.34639800
O	5.70319500	-0.18913600	0.67182800
O	6.55814800	2.29349000	-0.49907200
O	6.59671900	0.20958300	-1.90442700
O	4.81890500	2.01404500	-2.36099600
O	7.20822100	2.45536300	-2.97523800
O	5.38171100	4.50519100	-3.64706600
O	4.63034200	4.25982500	-0.95015700
O	2.00614500	3.83384200	-0.07129600

O	3.96127100	1.94077600	0.23171200
O	2.96242200	3.28517700	2.40761200
O	9.29358000	0.59467200	-2.74489700
O	8.63832200	0.38849600	-0.08637800
C	6.90247500	-0.46517300	-5.07435800
H	7.67394600	-1.00225200	-4.94087000
C	5.63362200	-0.93545800	-4.69594100
H	5.53864100	-1.79420400	-4.30330500
C	4.50517900	-0.11586700	-4.90708700
H	3.63969700	-0.43404200	-4.67521000
C	4.65520500	1.15356100	-5.45277500
H	3.89481200	1.71318200	-5.56310600
C	5.90060300	1.60680600	-5.83393500
H	5.98784000	2.46982900	-6.22256700
C	7.01713800	0.82299800	-5.65706600
H	7.86825800	1.14510900	-5.92623600
W	5.04024900	0.68037900	-0.68238500
W	5.87177600	3.72479100	-2.17452900
W	8.27149800	1.30418800	-1.52642100
pH7			
C	14.63532700	7.70455900	1.20761000
H	15.49748900	7.39486400	0.95827500
C	14.48188300	8.99290100	1.76275500
H	15.23123600	9.56502400	1.87593600
C	13.19948100	9.41101700	2.14518700
H	13.08602300	10.27439400	2.52622200
C	12.08693500	8.58838200	1.97795900
H	11.22114800	8.88602600	2.23614900
C	12.26772200	7.32213500	1.42418500
H	11.51605400	6.74960500	1.32160000

C	13.51075500	6.88192300	1.02256200
H	13.60882900	6.02566900	0.62194000
O	12.46000100	6.49100200	4.50146700
O	14.84898200	6.05588900	3.87367400
O	12.26568100	4.23895200	5.91331500
O	14.91980400	3.74775000	5.24988400
O	14.22329900	6.21735600	6.34646500
O	16.83274800	5.63437300	5.67069700
O	16.93233400	7.93741200	4.09436100
O	16.30011700	8.12097500	6.75905400
O	17.45305400	3.27864400	4.41236900
O	18.46000600	3.84803000	6.87419500
O	11.61824200	6.56238700	7.10996000
O	13.36957300	8.69206100	7.52940200
O	14.22732200	8.29604000	4.94695300
O	11.51366300	8.93851200	5.51717500
O	13.01784000	4.00269900	3.21709600
Ru	13.59747000	7.51368700	3.08674000
W	13.50752100	4.78896200	4.68665200
W	16.92707900	3.71562700	6.03284300
W	15.91679900	7.20927800	5.30553500
W	12.68357300	7.81588700	6.17402700
O	15.85534700	4.25934800	7.79395200
O	16.50278600	1.93591300	6.59730800
W	11.19394900	4.78267300	7.67442500
C	13.48570000	0.79374100	12.49965700
H	12.62353900	1.10343600	12.74899300
C	13.63914500	-0.49460100	11.94451300
H	12.88979200	-1.06672400	11.83133200
C	14.92154700	-0.91271700	11.56208000

H	15.03500500	-1.77609400	11.18104600
C	16.03409200	-0.09008200	11.72930900
H	16.89988000	-0.38772600	11.47111900
C	15.85330600	1.17616500	12.28308300
H	16.60497400	1.74869500	12.38566800
C	14.61027300	1.61637700	12.68470500
H	14.51219900	2.47263100	13.08532800
O	15.66102700	2.00729800	9.20580100
O	13.27204500	2.44241100	9.83359400
O	13.20122300	4.75055000	8.45738400
O	13.89772900	2.28094400	7.36080300
O	11.28828000	2.86392700	8.03657100
O	11.18869400	0.56088800	9.61290700
O	11.82091000	0.37732500	6.94821400
O	10.66797400	5.21965600	9.29489800
O	9.66102200	4.65027000	6.83307300
O	14.75145500	-0.19376100	6.17786600
O	13.89370600	0.20226000	8.76031500
O	16.60736500	-0.44021200	8.19009200
O	15.10318800	4.49560100	10.49017200
Ru	14.52355800	0.98461300	10.62052800
W	14.61350700	3.70933800	9.02061600
W	12.20422900	1.28902200	8.40173300
W	15.43745400	0.68241300	7.53324000
C	11.18577300	9.29204100	-1.20761000
H	10.32361100	9.60173600	-0.95827500
C	11.33921700	8.00369900	-1.76275500
H	10.58986400	7.43157600	-1.87593600
C	12.62161900	7.58558300	-2.14518700
H	12.73507700	6.72220600	-2.52622200

C	13.73416500	8.40821800	-1.97795900
H	14.59995200	8.11057400	-2.23614900
C	13.55337800	9.67446500	-1.42418500
H	14.30504600	10.24699500	-1.32160000
C	12.31034500	10.11467700	-1.02256200
H	12.21227100	10.97093100	-0.62194000
O	13.36109900	10.50559800	-4.50146700
O	10.97211800	10.94071100	-3.87367400
O	13.55541900	12.75764800	-5.91331500
O	10.90129600	13.24885000	-5.24988400
O	11.59780100	10.77924400	-6.34646500
O	8.98835200	11.36222700	-5.67069700
O	8.88876600	9.05918800	-4.09436100
O	9.52098300	8.87562500	-6.75905400
O	8.36804600	13.71795600	-4.41236900
O	7.36109400	13.14857000	-6.87419500
O	14.20285800	10.43421300	-7.10996000
O	12.45152700	8.30453900	-7.52940200
O	11.59377800	8.70056000	-4.94695300
O	14.30743700	8.05808800	-5.51717500
O	12.80326000	12.99390100	-3.21709600
Ru	12.22363000	9.48291300	-3.08674000
W	12.31357900	12.20763800	-4.68665200
W	8.89402100	13.28097300	-6.03284300
W	9.90430100	9.78732200	-5.30553500
W	13.13752700	9.18071300	-6.17402700
O	9.96575300	12.73725200	-7.79395200
O	9.31831400	15.06068700	-6.59730800
W	14.62715100	12.21392700	-7.67442500
C	12.33540000	16.20285900	-12.49965700

H	13.19756100	15.89316400	-12.74899300
C	12.18195500	17.49120100	-11.94451300
H	12.93130800	18.06332400	-11.83133200
C	10.89955300	17.90931700	-11.56208000
H	10.78609500	18.77269400	-11.18104600
C	9.78700800	17.08668200	-11.72930900
H	8.92122000	17.38432600	-11.47111900
C	9.96779400	15.82043500	-12.28308300
H	9.21612600	15.24790500	-12.38566800
C	11.21082700	15.38022300	-12.68470500
H	11.30890100	14.52396900	-13.08532800
O	10.16007300	14.98930200	-9.20580100
O	12.54905500	14.55418900	-9.83359400
O	12.61987700	12.24605000	-8.45738400
O	11.92337100	14.71565600	-7.36080300
O	14.53282000	14.13267300	-8.03657100
O	14.63240600	16.43571200	-9.61290700
O	14.00019000	16.61927500	-6.94821400
O	15.15312600	11.77694400	-9.29489800
O	16.16007800	12.34633000	-6.83307300
O	11.06964500	17.19036100	-6.17786600
O	11.92739400	16.79434000	-8.76031500
O	9.21373500	17.43681200	-8.19009200
O	10.71791200	12.50099900	-10.49017200
Ru	11.29754200	16.01198700	-10.62052800
W	11.20759300	13.28726200	-9.02061600
W	13.61687100	15.70757800	-8.40173300
W	10.38364600	16.31418700	-7.53324000

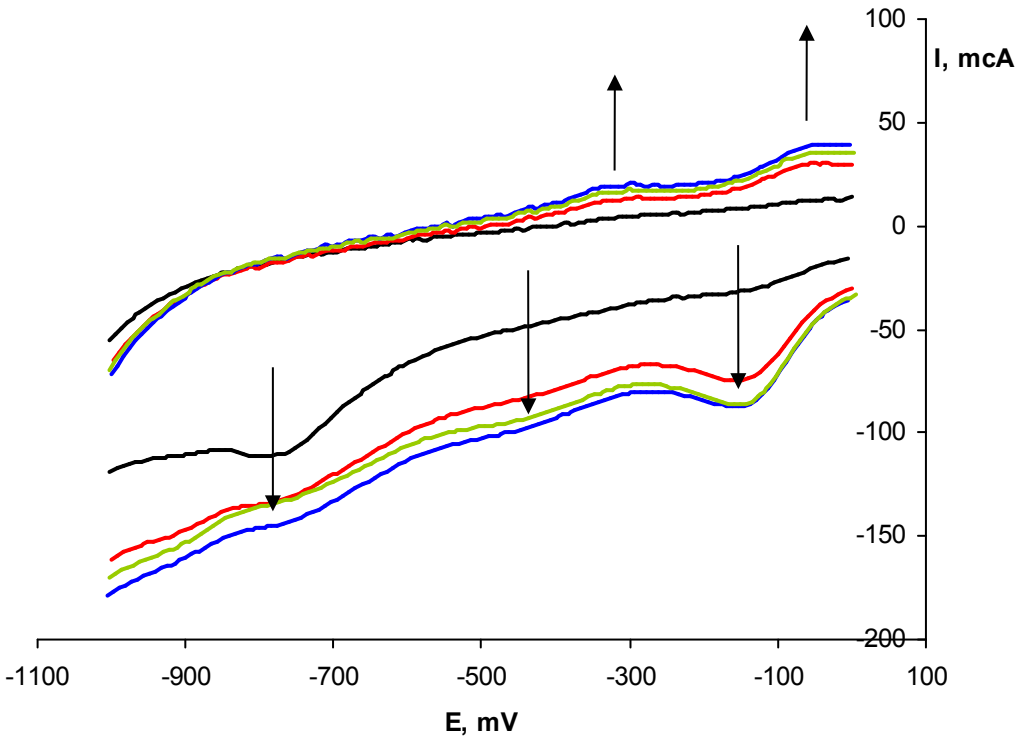


Fig. S8. Cathodic region of CV (an aqueous solution of 1 C = 0.008 M) in 0.5 M Li_2SO_4 at a scan rate of 10 mV/s with the addition of 100 µL of methanol at sequential cycling from 1 to 4 (from black to blue).